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# The Synthesis of Monoazo Pigments Derived from 5-(3'-Hydroxy-2'-Naphthoylamino)-Benzimidazol-2-One

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## *ABSTRACT*

*A new method of synthesizing benzimidazolone pigments by coupling in ethylene glycol has been developed. The properties of the pigment thus obtained have been examined and the influence of ethylene glycol on the process of formation of the pigment particles evaluated.*

## 1 INTRODUCTION

High fastness azo and polycyclic pigments are important pigments for use in the coloration of thermoplastics, car lacquers and high-quality printing inks. This group of pigments includes the diazo condensed pigments or the Cromophthal type (CIBA-GEIGY), and also monoazo pigments containing the cyclic carbamide system, such as benzimidazolone, as in the Permanent H and Hostaperm (Hoechst) pigments.

Condensed pigments are generally synthesized by acylation of 1,4-phenylenediamine and its derivatives with acid chlorides of monoazo dyes, using high-boiling organic solvents such as chlorobenzene and *o*-dichlorobenzene; this process thus involves solvent recovery costs. Benzimidazolone pigments have similar properties to those of condensed pigments.

The characteristics and properties of such pigments have been described in the literature.[1–5] They are normally synthesized by a two-stage method involving coupling diazotized aromatic amines with 5-aminobenzimidazolone derivatives, amides of 3-hydroxy-2-naphthoic acid or acetoacetic acid.

The products thus obtained are then heated in high-boiling polar solvents such as DMF, pyridine or nitrobenzene; it is also advisable that

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these reactions are carried out either in solutions or aqueous emulsions of organic solvents under pressure. In the course of this process the pigments acquire a crystalline form having high colour intensity and high fastness to light, organic solvents and heat.

Since the properties of the benzimidazolone pigments are dependent upon the conditions of synthesis and standardization, an investigation was undertaken to produce these pigments by a different method. A method for synthesizing benzimidazolone pigments by carrying out the coupling reaction and the standardization process in one stage is proposed, using a high-boiling, non-toxic, water miscible organic solvent.

It was found that ethylene glycol was a suitable solvent to meet these requirements. The synthesis of benzimidazolone pigments by coupling in ethylene glycol could be realized by various methods, e.g. by the action of solid diazonium salts or diazoamino compounds on glycol solutions of coupling components. However, this study shows that the most useful media are glycol solutions of diazonium salts obtained by diazotization of the aromatic amines in ethylene glycol using glycol nitrite.[6]

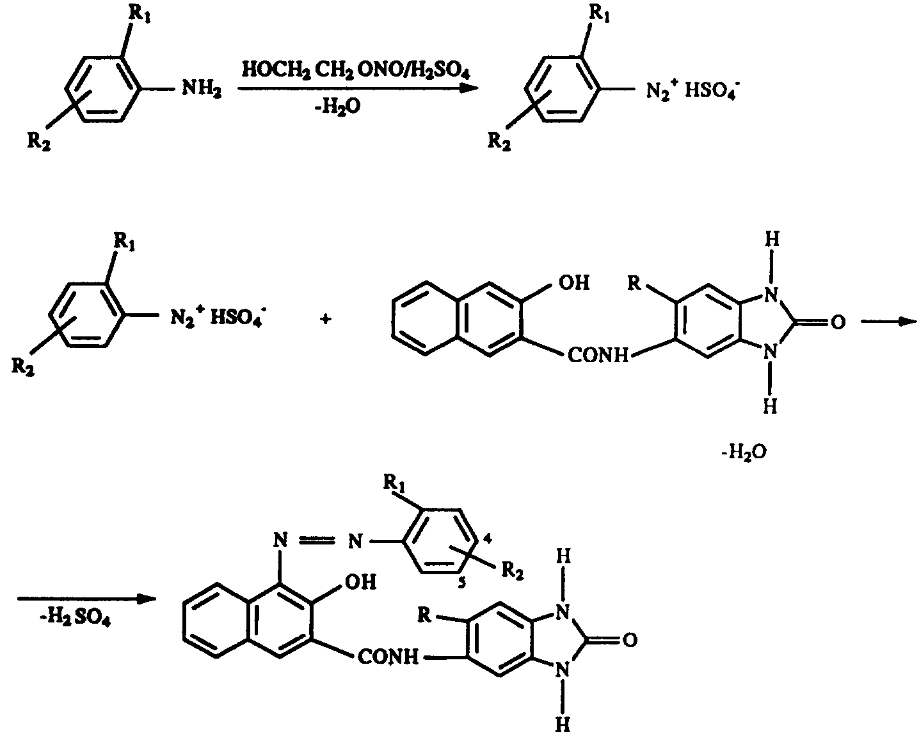
It was anticipated that the use of ethylene glycol would make it possible to carry out not only the coupling reaction but also the standardization of the pigments, without the necessity of isolating them from the reaction environment.

## 2 EXPERIMENTAL[7]

The synthesis of the benzimidazolone pigments (1) was carried out according to Scheme 1. 5-(3'-Hydroxy-2'-naphthoylamino)benizmidazol-2-one and its derivatives containing a chlorine atom or a methyl group (R = $CH_3$, Cl) in the benzimidazolone ring were used as coupling components; they were obtained by reaction of 3-hydroxynaphthoic-2 acid chloride with 5-aminobenzimidazolone or its derivatives, as previously described.[8]

The diazonium compounds used were: methyl (I) and *n*-butyl anthranilate (II), 2,5-dichloroaniline (III), 5-chloro-2-methylaniline (IV), 4-methyl-2-nitroaniline (V), 2-methyl-4-nitroaniline (VI), 2-methoxy-4-nitroaniline (VII), 4-methoxy-2-nitroaniline (VIII), 2-chloro-4-nitroaniline (IX), 4-chloro-2-nitroaniline (X), 3-amino-4-methoxybenzanilide (XI) and 3-amino-4-chlorobenzanilide (XII).

Diazonium salts of these amines were obtained in the form of glycol solutions by interaction of a 10% glycol nitrite solution in ethylene glycol with an amine solution in ethylene glycol, in the presence of sulphuric acid; sulphuric acid was used in excess according to the type of amine.



Scheme 1. Synthesis of benzimidazolone pigments: R = H, $CH_3$, Cl; $R_1$, $R_2$ = H, $CH_3$, Cl, $NO_2$, $OCH_3$, $COOCH_3$, COO (*n*-butyl), CONHPh.

This excess counteracts the formation of diazoamino compounds. The diazotization was carried out at 20–25°C.

Coupling was carried out at room temperature by adding the glycol solution of the diazonium salt to a solution of the coupling component in ethylene glycol, in the presence of sufficient potassium hydroxide to neutralize any excess of acid in the diazonium liquor.

After completion of the coupling reaction, the reaction mixture was heated for 1 h at 140–160°C, until a uniform image was observed in an optical microscope. The reaction mixture was then cooled to 100°C and diluted with hot water (30% volume). The pigment was filtered and the press cake washed with 50% aqueous ethylene glycol followed by hot water, and finally dried at 50–60°C.

The fastness of the pigments to light and organic solvents (ethanol, toluene, ethyl acetate) were determined according to PN 75/C-4702 and PN-71/C-4401; thermal properties of the pigments were tested using a Boetius' apparatus. The colour of the pigments was estimated visually in oil coatings containing 0·5 and 2·5% of the pigment with respect to the zinc oxide content. Results are given in Table 1.

### TABLE 1

Basic Parameters of the Synthesis of Benzimidazolone Pigments and Some of their Utility Properties

| *Pigment reference number* | *Structure of the pigment* | | | *Diazotization* | | *Yield (%)* | *Properties of pigments* | | | | *Colour of oil coat* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $R$ | $R_1$ | $R_2$[a] | *Type of amine* | $ArNH_2$[b] $H_2SO_4$ | | *Fastness to organic solvents* | | | *Fastness to light (1–8)* | |
| | | | | | | | *Ethanol* | *Toluene* | *Ethyl acetate* | | |
| C-1 | H | $COOCH_3$ | — | I | 1·5 | 80·7 | 5 | 5 | 5 | >6 | Red |
| C-2 | $CH_3$ | $COOCH_3$ | — | I | 1·5 | 80·8 | 4 | 5 | 4 | >6 | Bluish red |
| C-3 | Cl | $COOCH_3$ | — | I | 1·5 | 81·5 | 5 | 5 | 5 | >6 | Brown red |
| C-4 | H | COO(butyl) | — | II | 1·5 | 86·0 | 5 | 5 | 5 | >6 | Bluish red |
| C-5 | $CH_3$ | COO(butyl) | — | II | 1·5 | 80·2 | 4 | 5 | 4 | >6 | Bluish red |
| C-6 | Cl | COO(butyl) | — | II | 1·5 | 87·1 | 5 | 5 | 5 | >6 | Brown red |
| C-7 | H | Cl | $Cl^{(5)}$ | III | 1·5 | 91·5 | 5 | 5 | 5 | >6 | Brown |
| C-8 | H | $CH_3$ | $Cl^{(5)}$ | IV | 1·3 | 87·8 | 5 | 5 | 5 | >6 | Bluish red |
| C-9 | H | $NO_2$ | $CH_3^{(4)}$ | V | 2·0 | 89·2 | 5 | 5 | 5 | >6 | Reddish violet |
| C-10 | $CH_3$ | $NO_2$ | $CH_3^{(4)}$ | V | 2·0 | 88·7 | 5 | 5 | 4 | >6 | Reddish violet |
| C-11 | Cl | $NO_2$ | $CH_3^{(4)}$ | V | 2·0 | 91·0 | 5 | 5 | 5 | >6 | Brown red |
| C-12 | H | $CH_3$ | $NO_2^{(4)}$ | VI | 2·0 | 91·3 | 5 | 5 | 5 | >6 | Reddish violet |
| C-13 | H | $OCH_3$ | $NO_2^{(4)}$ | VII | 2·0 | 90·4 | 5 | 5 | 5 | >6 | Reddish violet |
| C-14 | H | $NO_2$ | $OCH_3^{(4)}$ | VIII | 2·0 | 93·8 | 5 | 5 | 5 | >6 | Reddish violet |
| C-15 | $CH_3$ | $NO_2$ | $OCH_3^{(4)}$ | VIII | 2·0 | 93·8 | 4 | 5 | 4 | >6 | Bluish violet |
| C-16 | Cl | $NO_2$ | $OCH_3^{(4)}$ | VIII | 2·0 | 91·5 | 5 | 5 | 5 | >6 | Reddish violet |
| C-17 | H | Cl | $NO_2^{(4)}$ | IX | 2·0 | 90·3 | 5 | 5 | 5 | >6 | Reddish brown |
| C-18 | H | $NO_2$ | $Cl^{(4)}$ | X | 2·0 | 89·2 | 5 | 5 | 5 | >6 | Reddish brown |
| C-19 | H | $OCH_3$ | $CONHPh^{(5)}$ | XI | 2·0 | 92·6 | 5 | 5 | 5 | >6 | Bluish red |
| C-20 | $CH_3$ | $OCH_3$ | $CONHPh^{(5)}$ | XI | 2·0 | 90·4 | 5 | 5 | 5 | >6 | Reddish violet |
| C-21 | Cl | $OCH_3$ | $CONHPh^{(5)}$ | XI | 2·0 | 87·5 | 5 | 5 | 5 | >6 | Bluish red |
| C-22 | H | Cl | $CONHPh^{(5)}$ | XII | 2·0 | 88·6 | 5 | 5 | 5 | >6 | Brown red |

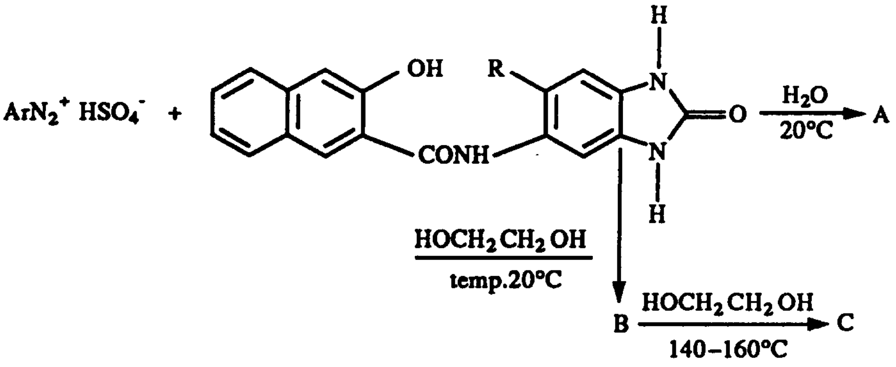
[a] Item number in aromatic amine ring (Scheme 1).

[b] Molar ratio.

**TABLE 2**
Properties of Benzimidazolone Pigments Synthesized by Different Methods

| *Structure of the pigment* | | *Pigment reference number* | *Fastness to organic solvents* | | | *Fastness to light* | *Relative intensity (%)* | *Texture* | *Average size of particles (μm)* |
|---|---|---|---|---|---|---|---|---|---|
| *R* | *$ArNH_2$* | | *Ethanol* | *Toluene* | *Ethyl acetate* | | | | |
| H | I | A-1 | 3 | 4 | 3 | 6 | 20 | Hard | 6·0 |
| | | B-1 | 4 | 5 | 4 | 6 | 25 | Hard | 2·0 |
| | | C-1 | 5 | 5 | 5 | 6 | 100 | Soft | 0·6 |
| H | II | A-4 | 4 | 4 | 4 | 4–5 | 15 | Hard | 4·0 |
| | | B-4 | 5 | 5 | 5 | 5 | 50 | Hard | 1·6 |
| | | C-4 | 5 | 5 | 5 | 6 | 100 | Soft | 0·1 |
| H | IV | A-8 | 3 | 3 | 3 | 6 | 20 | Hard | 3·0 |
| | | B-8 | 3 | 4 | 4 | 6 | 80 | Soft | 0·9 |
| | | C-8 | 5 | 5 | 5 | 6 | 100 | Soft | 0·4 |
| H | V | A-9 | 4 | 5 | 3 | 4 | 40 | Hard | 5·0 |
| | | B-9 | 4 | 4 | 4 | 5 | 50 | Hard | 1·3 |
| | | C-9 | 5 | 5 | 5 | 6 | 100 | Soft | 0·6 |
| H | XI | A-19 | 4 | 4 | 3 | 6 | 10 | Hard | 3·0 |
| | | B-19 | 5 | 5 | 4 | 6 | 40 | Hard | 0·8 |
| | | C-19 | 5 | 5 | 5 | 6 | 100 | Soft | 0·2 |
| H | XII | A-22 | 3 | 4 | 4 | 5 | 30 | Hard | 3·0 |
| | | B-22 | 4 | 5 | 4 | 6 | 40 | Soft | 0·6 |
| | | C-22 | 5 | 5 | 5 | 6 | 100 | Soft | 0·1 |

A—Coupling in Water; B—Coupling in Ethylene Glycol; C—Coupling and Heating in Ethylene Glycol.



**Scheme 2.** Aqueous coupling (A pigments), coupling in ethylene glycol without heating (B pigments), and coupling and heating in ethylene glycol (C pigments).

Further experiments were carried out to evaluate the influence of ethylene glycol on the particle size of the pigments; its influence can occur during the coupling process as well as during the standardization (heating) process.

To investigate this, comparative syntheses were carried out for the selected benzimidazolone pigments, viz. aqueous coupling (A pigments), coupling in ethylene glycol without heating (B pigments) and coupling and heating in ethylene glycol (C pigments) (Table 2, Scheme 2).

The resulting pigments were assessed for colour intensity, texture, and fastness to organic solvents and light; results are shown in Table 2.

The powder pigments synthesized by methods A, B and C were also studied using a TESLA BS-250 electron microscope.

Synthesis of the pigment C-14 illustrates the method used. A 10% solution of glycol nitrite in ethylene glycol (9·5 g) was added dropwise at 20°C to a solution of 4-methoxy-2-nitroaniline (1·67 g) in 96% sulphuric acid (2·94 g) and of ethylene glycol (30 cm$^3$) and the reaction mixture was stirred for 0·6 h. The diazonium salt thus obtained was added over 30 min at 20°C to a solution of 5-(3'-hydroxy-2'-naphthoylamino)benzimidazol-2-one (3·19 g) and potassium hydroxide (1·85 g) in ethylene glycol (90 cm$^3$). After stirring for 1 h acetic acid (0·3 g) was added and the mixture heated to 140–150°C for 1 h. After cooling to 100°C, hot water (40 cm$^3$) was added and the pigment filtered while hot. The press cake was washed with 50% aqueous ethylene glycol until the filtrate was clear, and then with hot water, prior to drying at 50–60°C; yield was 4·8 g (93·8%).

The remaining pigments were obtained in an analogous manner.

## 3 RESULTS AND DISCUSSION

The pigments were obtained using the described method in good yields and high purities. From the investigations on the pigment properties, it was found that the fastness of the benzimidazolone pigments to light and organic solvents was relatable to the nature of the coupling component and to the presence of the benzimidazolone system in it. All pigments, irrespective of the structure of the diazonium component, showed light fastness above 6. The pigments were also found to be highly resistant to typical organic solvents such as ethanol, toluene and ethyl acetate, with the exception of pigments C-2, C-5, C-10 and C-15, which had a slightly lower resistance to ethanol and ethyl acetate. This is relatable to the presence of the methyl group in the benzimidazolone ring, which can have an adverse influence on the formation of the stable crystalline form.

The pigments did not melt up to 360°C, but small changes in the colour of the heated powders were observed at temperatures above 340–350°C.

The pigments obtained by this new method had a soft to very soft texture, which facilitates their dispersion in organic binders.

The colour properties of the pigments are highly dependent upon the nature of the diazo component, although the influence of the substituent in the benzimidazolone ring is also evident. The presence of a chlorine atom in the latter results in a small hypsochromic shift, and that of a methyl group a bathochromic shift.

However, the influence of these groups on the colour of the pigments has little practical significance, since similar or even greater changes in colour can be achieved by appropriate choice of the diazo component. The benzimidazolone pigments, for example, can be produced in a wide range of shades using only one coupling component, i.e. 5-(3'-hydroxy-2'-naphthoylamino)benzimidazol-2-one; this gives, with different diazotized aniline and benzanilide derivatives, pigments of different shades, e.g. reds with a blue shade (C-4, C-8, C-19), violets (C-9, C-12, C-13, C-14) and brown (C-7).

The good properties of the benzimidazolone pigments obtained by applying the new synthetic method confirmed the usefulness of ethylene glycol as solvent in the synthesis of pigments of this type. The influence of ethylene glycol on the properties of the benzimidazolone pigments was assessed by comparing the products obtained using methods A and B. It was found that the A pigments, synthesized by aqueous coupling, had considerably poorer properties in comparison with analogous pigments obtained by method C. The fastness to organic solvents, and the intensity of colour, was significantly lowered. The A-type pigments were also characterized by a hard texture, which makes their dispersion in binders more difficult. Differences in light fastness were also apparent; the 'A' pigments had 1–2 points lower fastness to light relative to analogous pigments obtained by method C.

The pigments obtained by method B showed properties intermediate between those of the A- and C-derived pigments, particularly with respect to fastness to organic solvents.

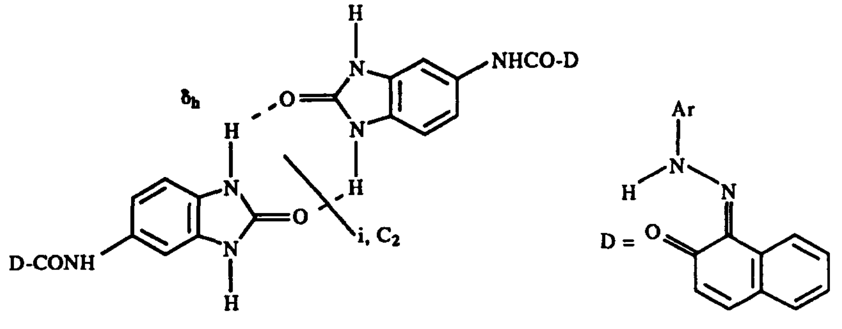
These results confirm the beneficial influence of ethylene glycol in the coupling stage, as well as in the heating process, when the required crystalline form is obtained.

Electron microscope data confirmed this proposition. The A pigments, synthesized in aqueous medium appeared in the form of large, irregular agglomerates (1·2–6 μm), while the B pigments, synthesized in ethylene glycol, were usually small regular agglomerates of crystalline particles (0·3–2 μm) shaped, for example, as needles. The C pigments appeared as well-dispersed, fine crystalline particles (0·1–0·8 μm) with a clearly defined shape.

It was also observed that the A pigments showed no advantageous change in their crystalline form, nor any significant improvement in their end-use properties as a result of prolonged heating in ethylene glycol.

However, the B pigments, synthesized by coupling in ethylene glycol, were quite readily transformed during heating in ethylene glycol into the C form, characterized by very good end-use properties.

These results, and the data pertaining to the crystalline structure of one of the benzimidazolone pigments, viz. *n*-butyl anthranilate → 5-(3'-hydroxy-2'-naphthoylamino)benzimidazol-2-one,[2] enables a mechanism for the formation of these pigments to be proposed. During the initial stage associates are most probably formed as dimers with hydrogen bonding to the amido groups (Scheme 3); the dimers then undergo further association, forming crystals. The dimers have a very advantageous structure with respect to the formation of stable crystalline



**Scheme 3.** Synthesis of benzimidazolone pigments in ethylene glycol.

structures, i.e. they have a flat and linear configuration, with elements of symmetry ($\delta_h$, $i$, $C_2$), which renders possible their very compact packing in the crystal lattice. As a result, intermolecular action increases, which, in turn, determines the fastness parameters of the pigments.

In the series of pigments studied, the formation of the symmetrical dimers governs their fastness, and also explains why used relatively simple monoazo pigments exhibit properties normally associated with high-fastness pigments.

It is essential, during the synthesis or standardization of the pigments, that highly crystalline products are formed. The synthetic method described here for the synthesis of benzimidazolone pigments in ethylene glycol meets this requirement, as is confirmed by the high fastness of the pigments to light and organic solvents. The very soft texture of the pigments thus obtained ensures their facile dispersibility in coloured materials such as lacquers and thermoplastics.

The synthetic method used here for benzimidazolone pigments may be more generally applicable to azo pigments generally, and could be used, for example, in the synthesis of monoazo pigments derived from Naphtol-AS. In this case also, the pigments obtained possess better properties than those synthesized using an aqueous coupling medium, and the products are obtained in very high purity. These pigments, can therefore be used in areas where high purity requirements are essential, e.g. in food packaging, cosmetics, etc.

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